

# **Quantitative Chemical Mass Transfer in Coastal Sediments During Early Diagenesis: Effects of Biological Transport, Mineralogy, and Fabric**

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## **LONG-TERM GOAL**

Our long term goals are to provide a better quantitative and mechanistic understanding of chemical processes that occur in fine-grained coastal and continental margin marine sediments, especially with regard to how these processes affect biogeochemical fluxes and the transport and/or retention of environmentally sensitive natural and anthropogenically generated chemical compounds in coastal environments.

## **OBJECTIVES**

The objective of this project is to make better predictions of chemical mass transfer in fine-grained siliciclastic coastal sediments, especially with regard to the impact of biologically-enhanced transport and the effects of sediment mineralogy, fabric, and particle surface chemistry on the fluxes of biochemical species and pollutants in coastal marine sediments. Production of a computer code is a prime objective.

## **APPROACH**

Our approach combines the strengths of investigators from three institutions, Scripps Institution of Oceanography (SIO), The Naval Research Laboratory at the Stennis Space Center (NRL), and Georgia Technological University (GTU). This consortium is working together to integrate controlled laboratory experiments on chemical transport processes in model sediments (SIO) with field-based biogeochemical studies and sediment fabric/microfabric characterizations (NRL) and numerical reactive transport modeling (GTU). The overall objectives for this time period are to determine mechanisms of mineral-bio-organic interactions in fine-grained siliciclastic sediments and to upgrade STEADYSED, a multicomponent numerical model of reactive transport in aquatic sediments. To this end our consortium will carry out pulse tracer experiments and O<sub>2</sub> micro-profiling in bioturbated coastal sediments, (2) perform high-resolution imaging of sediment fabric and statistical analysis of burrow networks at the same field sites, (3) develop, characterize, and implement laboratory reactor systems and model sediment packs, (4) investigate interactions of common coastal sediment minerals with the dissolved and colloidal organic components in seawater, (5) develop stochastic models for burrowing, and biological particle mixing, and (6) derive general exchange functions for solute and solid transport by macrofauna,

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## WORK COMPLETED

For the SIO-directed part of the program, materials for the reactors have been purchased and the first reactor prototype is under construction. Construction of the filtering system for the organic and seawater adsorption experiments is under way. All equipment for high precision porosity measurements have been purchased and calibrated. Mineralogic starting materials (illite, chlorite, quartz silt, and kaolinite) have been purchased and are undergoing surface area, surface site, and chemical characterization. The organic adsorption experiments are designed and within a month of being implemented.

An important new model of organic carbon preservation in fine-grained continental margin sediments has been deduced from microfabric and mineralogical data from fine-grained continental margin siliciclastic sediments. The new model indicates a large role is played by sediment microfabric and clay mineralogy. Using the NRL data base of sediment microfabric photomicrographs, the relationship between minerals and microbes in fine-grained sediments has been examined, synthesized, and written up. The results are accepted for publication. The amount of pore space occluded by organic matter in sediments of organic carbon contents ranging up to 5 wt% organic carbon has been estimated and its potential impact on flux calculations in fine-grained sediment diffusive transport systems has been assessed. A correction to the water content and porosity of fine-grained sediments containing smectite, a hydrated mineral with 25 wt percent intracrystalline H<sub>2</sub>O that is easily released upon drying, has been devised and tables of correction values prepared. A paper on the results of the effects of organic matter and smectite on sediment porosity calculations is in preparation. Analysis of phosphorous data from fine-grained continental margin sediment solids and pore waters has been completed and estimates have been made regarding the amount of authigenic francolite precipitation on continental margins and its impact on the global P budget.

## RESULTS

**A.** Our present work shows organic carbon in sediments deposited on open continental slopes off western North America appears to be strongly controlled by sediment microfabric, resulting from the interaction of organic matter, living and dead, with clay minerals. Different clay suites appear to have different capacities for retaining organic carbon. Within a single suite of clay minerals, these relations appear to be linearly correlated. This finding has important implications for studies of sediment physical properties, as well as theoretical and numerical models of sediment particle interaction because the presence of organic matter on clay mineral surfaces will significantly affect their surface properties and layer charge potentials. Organic and textural associations controlled by the clay mineral suite may also significantly impact the bioavailability of organic matter for benthic fauna, diffusional fluxes of biogeochemical species, and the porosity evolution of the sediment. These aspects are presently under further investigation.

**B.** Study of photomicrographs of the microfabric and textural relations of organic matter, minerals, and microbes in fine-grained siliciclastic sediments shows that relatively robust microaggregates generally < 25 µm or less in diameter appear to be characteristic of marine sediments. Our sample treatments and preparations show these aggregates to be moderately resistant to dispersal in water and composed of minerals, organic remains, microbes, and microbial secretions. These aggregates are similar in character to those developed in marine snow traveling in the nepheloid layer just above the sea floor. We suggest that the nepheloid layer marine aggregates provide the baseline for understanding the

preservation of organic carbon in continental margin sediments and the evolution and *in situ* distribution of sedimentary organic matter. Our study indicates that for oxic and suboxic continental margins, models of organic carbon deposition should include provisions for lateral transport of organic matter and its possible extended residence time in near-seafloor, oxygenated, aerobic environments. During such intervals, organic matter would be repeatedly cycled between surface sediments and the overlying bottom water, being moved down slope from its initial point of impact with the seafloor to its site of ultimate burial and removal from the carbon cycle. It seems likely that such a process would increase significantly the refractory character of the organic matter, thus reducing its bioavailability to benthic fauna.

**C.** Microbes, their exocellular secretions, and their impact on the mineralogy and microfabric of fine-grained continental margin sediments were also investigated and photomicrographs of characteristic mineral-microbe associations within the first meter of burial beneath the seafloor at conditions ranging from aerobic to anaerobic were studied. Our analysis shows that the bacterial habitation of marine sediments has a significant impact on the evolution of sediment physical properties and a potential major influence on fine-grained sediment chemical transport. Analysis of TEM images show the presence of single-celled prokaryotes, prokaryotic colonies, and eukaryotic organisms, as well as motile, sessile, and predatory species. Bacterial cells dominate the assemblage. The most commonly observed mineral-biological interaction is the surrounding, or close association of isolated heterotrophic bacterial cells by clay minerals. Almost without exception, the external surfaces of the bacteria are covered with secreted exocellular slimes composed of cross-linked polysaccharide fibrils. These fibrils act to bind sediment grains into relatively robust microaggregates (roughly 25  $\mu\text{m}$  or less in diameter) and can significantly impact the interaction between microbes and minerals, as well as the chemical and physical transport of fluids and dissolved aqueous species through the sediment. Although pore water chemical profiles from the field sites described below have abundant dissolved Fe and Mn, no close association was found between the microbes imaged and precipitated metal oxyhydroxides or other authigenic minerals, such as commonly reported from laboratory cultures.

**D.** In addition to acting as sediment binding agents, organisms, their exudates, and sedimentary organic detritus contain significant amounts of internal  $\text{H}_2\text{O}$ . Much of this  $\text{H}_2\text{O}$  can be released, along with the water in interstitial pore spaces, when coastal and continental margin sediments are dried for studies of sediment physical properties. Unless  $\text{H}_2\text{O}$  lost from organic phases during the drying process is explicitly partitioned back into the organic phases, it will be implicitly included in the water content of the sediment and any estimations of interstitial pore volume (e.g., porosity and void ratio). Thus, the water content, porosity, and void ratio of organic-bearing sediments, calculated in the traditional manner (i.e., assuming the mass of  $\text{H}_2\text{O}$  lost upon drying is from pore water residing in intergranular pore spaces) may not represent a true assessment of free liquid (i.e., pore water) in intergranular spaces (Table 1). A similar situation exists for physical properties and fluxes derived from sediments containing smectites and zeolites, common hydrated sedimentary minerals that contain significant amounts of internal crystallochemical  $\text{H}_2\text{O}$  which is released upon drying (Table 2). In addition to affecting porosity determinations, microbes, clay minerals, and organic material also impact sediment chemical and fluid transport when they are present in pores or fluid escape channels because they can decrease sediment hydraulic conductivity by increasing the tortuosity. Results of our calculations indicate that the  $\text{H}_2\text{O}$  content of organic matter significantly affects (i.e., variations of the uncorrected porosity values from the corrected porosity values of  $\sim 10\%$  or more) the reported porosity values for sediments with true porosities of 75% or less (Table 1). When organic carbon contents are high (i.e.,  $>5$  wt %) and porosities are low (65-55%) differences between traditionally calculated porosity values and those

corrected for the H<sub>2</sub>O in organic matter can be as much as 25%. A similar situation exists when porosity values reported from smectite-bearing sediments are not corrected for the H<sub>2</sub>O that resides in the smectite interlayer (Table 2).

**Table 1. Calculated Volume of Pore Water and Volume of Sediment Solids  
(i.e., Minerals plus Organic Matter) Per 100 g of Sediment.**

Porosity (%)	Organic Carbon (wt %)	V <sub>pore water</sub> (cm <sup>-3</sup> )	V <sub>minerals</sub> (cm <sup>-3</sup> )	V <sub>hydrated OM</sub> (cm <sup>-3</sup> )	V <sub>sediment</sub> (cm <sup>-3</sup> )	OM <sup>e</sup> (vol %)	Δφ (%)
55	1	46 - 49	35 - 37	2 - 3	83 - 89	2.5 - 3.4	5 - 6
55	2	47 - 51	34 - 36	4 - 6	85 - 93	4.9 - 6.5	8 - 12
55	3	49 - 53	33 - 35	6 - 9	88 - 97	7.0 - 9.3	13 - 17
55	4	50 - 56	32 - 34	8 - 12	90 - 102	9.2 - 11.8	17 - 21
55	5	51 - 58	31 - 33	10 - 15	92 - 106	11.2 - 14.2	20 - 26
65	1	70 - 74	35 - 37	2 - 3	107 - 114	2.0 - 2.6	3 - 4
65	2	72 - 77	34 - 36	4 - 6	110 - 119	3.8 - 5.0	6 - 8
65	3	74 - 81	33 - 35	6 - 9	113 - 125	5.5 - 7.2	8 - 11
65	4	76 - 85	32 - 34	8 - 12	116 - 131	7.1 - 9.2	11 - 14
65	5	78 - 89	31 - 33	10 - 15	119 - 137	8.7 - 11.0	13 - 17
75	1	112 - 119	35 - 37	2 - 3	149 - 159	1.4 - 1.9	2 - 3
75	2	116 - 125	34 - 36	4 - 6	154 - 167	2.7 - 3.6	4 - 5
75	3	119 - 131	33 - 35	6 - 9	158 - 175	3.9 - 5.2	5 - 7
75	4	122 - 137	32 - 34	8 - 12	162 - 183	5.1 - 6.6	7 - 9
75	5	126 - 143	31 - 33	10 - 15	167 - 191	6.2 - 7.9	8 - 11
85	1	212 - 225	35 - 37	2 - 3	249 - 265	0.8 - 1.1	1
85	2	219 - 236	34 - 36	4 - 6	257 - 278	1.6 - 2.2	2 - 3
85	3	224 - 247	33 - 35	6 - 9	263 - 291	2.3 - 3.1	3 - 4
85	4	231 - 259	32 - 34	8 - 12	272 - 305	3.1 - 3.9	4 - 5

85	5	237 - 270	31 - 33	10 - 15	278 - 318	3.7 - 4.7	4 - 6
95	1	712 - 755	35 - 37	2 - 3	749 - 795	0.3 - 0.4	<1
95	2	733 - 792	34 - 36	4 - 6	771 - 834	0.5 - 0.7	1
95	3	753 - 830	33 - 35	6 - 9	792 - 874	0.8 - 1.0	1
95	4	774 - 868	32 - 34	8 - 12	814 - 914	1.0 - 1.3	1
95	5	795 - 905	31 - 33	10 - 15	836 - 953	1.2 - 1.6	1 - 2

Note: In all columns containing two numbers separated by a hyphen, the first number refers to the minimum calculated value and the second to the maximum calculated value with maxima and minima being determined by maximum and minimum values adopted for the average sediment bulk density ( $2.65 - 2.75 \text{ g cm}^{-3}$ ) and maximum and minimum values of the density of sediment organic matter ( $0.9 - 1.3 \text{ g cm}^{-3}$ ). <sup>a</sup> Range of the volume of pore water compatible with the total solid volumes calculated for 100 g of dry sediment. <sup>c</sup> Minimum value for the total reconstructed volume (minerals plus organic matter plus pore water) of the 100 g dry sediment sample. <sup>d</sup> Maximum value for the total reconstructed sediment volume (minerals plus organic matter plus pore water) of the 100 g dry sediment sample. <sup>e</sup> Percent of the pore water volume that is occupied by hydrated organic matter in the reconstructed sediment.

**Table 2. Effect of hydrated smectite on the porosity of smectite-bearing sediment samples.**

Smeectite <sup>1</sup> (vol %)	$\Delta\phi$ (%) <sup>a</sup> $\phi_t = 50$	$\Delta\phi$ (%) <sup>a</sup> $\phi_t = 55$	$\Delta\phi$ (%) <sup>a</sup> $\phi_t = 60$	$\Delta\phi$ (%) <sup>a</sup> $\phi_t = 65$	$\Delta\phi$ (%) <sup>a</sup> $\phi_t = 70$	$\Delta\phi$ (%) <sup>a</sup> $\phi_t = 75$	$\Delta\phi$ (%) <sup>a</sup> $\phi_t = 80$	$\Delta\phi$ (%) <sup>a</sup> $\phi_t = 85$	$\Delta\phi$ (%) <sup>a</sup> $\phi_t = 90$	$\Delta\phi$ (%) <sup>a</sup> $\phi_t = 95$
100	37 - 46	30 - 38	25 - 31	20 - 25	16 - 20	12 - 15	9 - 15	6 - 12	4 - 5	2
90	33 - 42	27 - 34	22 - 28	18 - 23	14 - 18	11 - 14	8 - 14	6 - 10	4 - 5	2
80	29 - 37	24 - 30	20 - 25	16 - 20	13 - 16	10 - 12	7 - 12	5 - 9	3 - 4	2
70	26 - 33	21 - 27	17 - 22	14 - 18	11 - 14	9 - 11	6 - 11	5 - 8	3 - 4	1 - 2
60	22 - 28	18 - 23	15 - 19	12 - 15	9 - 12	7 - 9	6 - 9	4 - 7	2 - 3	1
50	18 - 23	15 - 19	12 - 15	10 - 13	8 - 10	6 - 8	5 - 8	3 - 6	2 - 3	1
40	15 - 19	12 - 15	10 - 12	8 - 10	6 - 8	5 - 6	4 - 6	3 - 5	2	1
30	11 - 14	9 - 11	7 - 9	6 - 8	5 - 6	4 - 5	3 - 5	2 - 3	1 - 2	1
20	7 - 9	6 - 8	5 - 6	4 - 5	3 - 4	2 - 3	2 - 3	1 - 2	1	0
10	4 - 5	3 - 4	2 - 3	2 - 3	2 - 2	1 - 2	1 - 2	1	0 - 1	0
5	2 - 2	2	1 - 2	1	1	1	1	0 - 1	0	0
2	1	1	1	1	0	0	0	0	0	0
1	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0

<sup>1</sup>Volume % smectite in the wet sample; <sup>a</sup>Percent change in the volume between the true porosity ( $\phi_t$ ) and the apparent (i.e., uncorrected) porosity (i.e.,  $\phi_t$  plus the volume of the hydrated smectite interlayers).

E. Sediment and porewater data on phosphorous in fine-grained, siliciclastic, continental margin sediments indicates that the authigenic mineral Francolite is actively forming in the uppermost few meters of the sediment column. This P-bearing mineral is being formed at the expense of phosphorous bound in organic matter and to Fe-oxyhydroxides. If the formation rate of Francolite on the California margin is representative of continental margins overall, this results in a sink of  $1.9 \pm 0.8 \times 10^{10} \text{ mol P yr}^{-1}$ , which is about 35% of the yearly global input flux of reactive P to the ocean.

## **IMPACT/APPLICATION**

The new microfabric model for organic matter preservation is a potentially major breakthrough in the study of organic carbon preservation. It unifies previously disparate data sets and reconciles conflicting conclusions arrived at from interpretations of similar data sets under different sets of environmental conditions (such as sedimentation rate and biological productivity). This model has already attracted significant attention from both the marine and soil science communities. The water content/porosity corrections that have been produced permit more accurate estimates of chemical fluxes in and out of fine-grained organic carbon and/or smectite-rich coastal sediments.

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